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Nano-Sized [60]Fullerene-Cyclodextrin Molecules

Jeong-Seo Park, Han-Chang Kang, and Kurt E. Geckeler*
Laboratory of Applied Macromolecular Chemistry,
Department of Materials Science and Engineering,
Kwangju Institute of Science and Technology,
1 Oryong-dong, Buk-gu,
Kwangju 500-712, South Korea

ABSTRACT

As [60]fullerene is a very hydrophobic macromolecule, there have been a number of attempts to make it more hydrophilic for biomedical applications. By attaching hydrophilic moieties such as poly(oxyethylene)(POE) chains and cyclodextrin molecules to [60]fullerene, novel water-soluble and biocompatible materials have been successfully prepared [1,2].

The synthesis of novel macrocyclic fullerene conjugates which are water-soluble is reported. The telechelic fullerene derivatives have been prepared *via* addition reaction of POE-based arms with covalently bonded β-cyclodextrin (CD) to [60]fullerene. To this end, a mono-tosylated CD derivative has been prepared in pyridine and then reacted with an amino-functional POE in the presence of triethylamine. The subsequent reaction of [60]fullerene with the hydrophilic POE-conjugated CD-derivative yielded the macrofullerene after separation and purification procedures.

The macrocyclic [60]fullerene derivatives obtained were soluble in water and characterized by UV-VIS and FT-IR spectroscopy as well as light scattering measurements and thermogravimetric analysis.

INTRODUCTION

Since [60]fullerene has been made preparatively accessible [3], the promising properties of [60]fullerene stimulate an increasing interest for fullerene-containing polymers in view of biomedical applications [1,2]. There have been a number of attempts to make it more hydrophilic, as [60]fullerene possesses radical scavenging effects [4].

POE exhibits the minimal interfacial energy in an aqueous environment and an unique solubility in water. Furthermore, as POE is a very hydrophilic and biocompatible material, it is already applied in many fields such as biomedical and pharmaceutical areas [5]. And CD are water-soluble cyclic oligosaccharides built up of glucopyranose units. Thus, by using of [60]fullerene as a molecular core in linking multiple POE chains and CD molecules novel water-soluble and biocompatible materials have been successfully prepared.

EXPERIMENTAL DETAILS

The synthetic procedure consists of three steps. The first step is the preperation of mono-6-(p-tolylsulfonyl)-β-cyclodextrin (m-TsCD). m-TsCD was synthesized by following a standard procedure [6].

The second step was the preparation of mono-poly(oxyethylene)-β-cyclodextrin (POE-CD). It was synthesized by reacting equimolar quantities of m-TsCD and difunctional amino POE (aPOE) with a molecular mass 2 kg mol^{-1}.

In the final step, we synthesized the (aPOE)-poly(oxyethylene)-β-cyclodextrin (F-(POE-CD)$_n$) by reacting with POE-CD and [60]fullerene. During the reaction, the color of solution changed from purple to light-yellow, and then to pink.

UV/Vis spectra were obtained with a UV/Visible spectrometer (Perkin Elmer, Lambda 12). The particle size was measured by dynamic light scattering (Malvern Instruments Ltd. Series 4700) with argon ion laser system at 488 nm with a digital correlator.

RESULTS AND DISCUSSION

The macrocyclic [60]fullerene derivatives obtained were soluble in water and the synthesis of these conjugates was confirmed by UV-VIS Spectroscopy.

In Figure 1. it is shown that the [60]fullerene-POE conjugate absorbs in the UV-visible region showing a maximum at 250-270 nm. At higher wavelengths, the absorbance presents a smoothly decreasing shoulder without characteristic maxima. As the reaction proceeded, the peak height at around 340 nm decreased and finally disappeared. This phenomena explains the disruption of the π-bonds of [60]fullerene due to the formation of side arms which are covalently bonded to [60]fullerene.

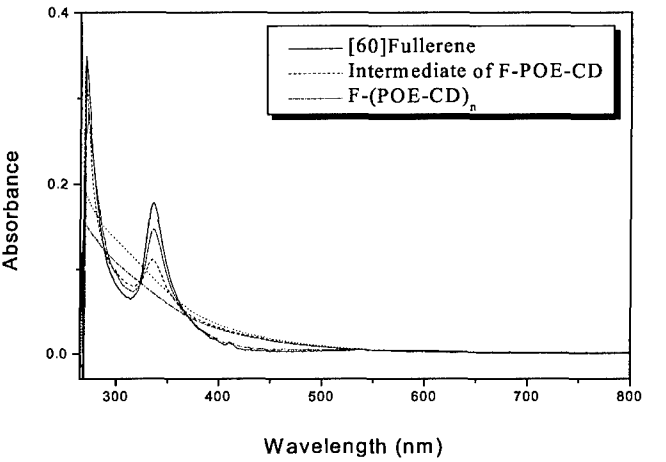

Figure 1. UV/VIS spectra showing the formation of [60]fullerene-cyclodextrin conjugates (F-(POE-CD)$_n$) by an addition reaction with reaction time

The infrared spectrum of the polymer is shown in Figure 3. It looks similar to that of the POE-CD prepolymer. A broad band around 3440 cm^{-1} corresponding to the absorption of primary and secondary amine and alcohol groups of CD is shown. It also shows a sharp peak at around 1100 cm^{-1}. Interestingly the two peaks around 520 cm^{-1} and 570 cm^{-1} , shown in both [60]fullerene and POE-CD, changed their forms to broad bands.

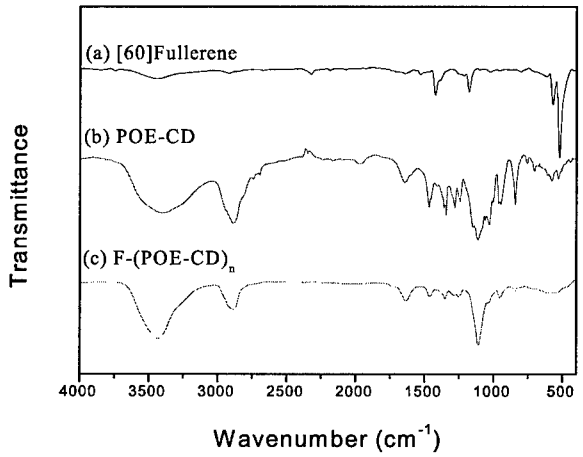

Figure 2. FT-IR spectra of (a) [60]fullerene , (b) POE-CD, and the reaction product (c) F-(POE-CD)$_n$

Figure 3 shows the particle size distribution of F-(POE-CD)$_n$ obtained by laser light scattering. The molar mass thus obtained was 13,496 g mol^{-1} and the average particle size in water was 24.6 nm with a mean value distribution of 98.7%. This value is a little smaller than the expected whole length of fully extended fullerene derivatives. Based on the thermo-gravimetric analysis, an average number of 2.07 side-arms could be calculated.

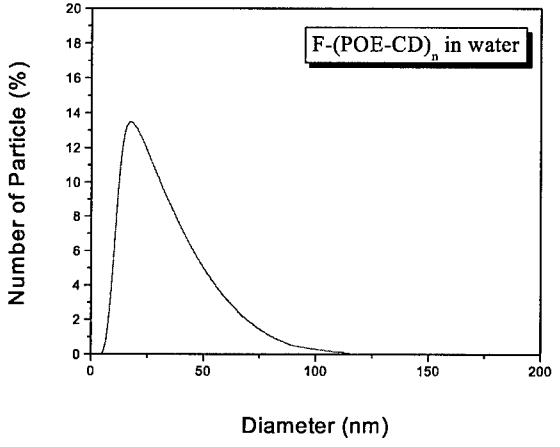

Figure 3. Particle size distribution of F-(POE-CD)$_n$ by laser light scattering

The characteristic properties such as hydrophilicity and expected biocompatibility of this novel macrocyclic molecules hold promise for a broad range of biomedical applications [7,8].

CONCLUSIONS

The synthesis of a novel water-soluble macrocyclic [60]fullerene conjugate is described. The macromolecules were prepared by the multiple addition of POE arms with covalently bonded CD to [60]fullerene. The preperation of the [60]fullerene conjugates by the addition of hydrophillic POE and CD is a useful method of imparting water-solubility of [60]fullerene derivatives.

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